BERRY PHASE AND THE SYMMETRY OF THE VIBRONIC GROUND STATE IN DYNAMICAL JAHN-TELLER SYSTEMS

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Due to the frequent presence of a Berry phase, in most cases of dynamical Jahn-Teller systems the symmetry of the ground state is the same as that of the electronic state. However, the $H \otimes h$ icosahedral case, relevant for the physics of fullerene ions, provides a first example of linear coupling leading, at strong coupling, to a change in symmetry of the ground state to a totally symmetric nondegenerate state. We generalize this observation and show through detailed examples that the absence of a Berry phase can, but does not necessarily, lead to a nondegenerate ground state.

The traditional field of degenerate electron-lattice interactions (Jahn-Teller effect) in molecules and impurity centers in solids[1,2] has attracted new interest in recent years, excited by the realization of new systems which call for a revision of a number of commonly accepted beliefs. A whole range of icosahedral molecular systems including C_{60} ions and some higher fullerenes, thanks to the rich structure of the symmetry group, are characterized by up to fivefold-degenerate representations of the electronic and vibrational states of the isolated molecule/ion. Novel Jahn-Teller (JT) systems have therefore been considered theoretically,[2,3,4] disclosing intriguing features,[4,5,6,7,8] often related to the rôle of a Berry phase[9] in the coupled dynamics.

As it is well known, the molecular symmetry, reduced by the JT distortion with the splitting of the electronic-state degeneracy, is restored when the coherent tunneling between equivalent distortions is considered, in the dynamical Jahn-Teller (DJT) effect. In this context it was commonly accepted an empirical "symmetry conservation rule", sometimes referred to as "Ham's theorem", stating that the symmetry of the vibronic DJT ground state, at all coupling strengths, remains the same as that of the electronic multiplet prior to coupling:[2] all linear JT systems known till a few years ago, for single-electron occupancy, systematically satisfy this empiric rule. It was understood recently that this phenomenon, not automatically implied by the DJT physics, is in reality a fingerprint of a Berry phase[9] in the entangled electronic-phononic dynamics.[4,7,10] Consequently, this geometrical phase appeared as a universal feature of the DJT systems.

In this context, it came unexpected the discovery of the first linear JT

system showing a *nondegenerate ground state* in the strong-coupling limit.[7,8] This result was demonstrated for the model that in spherical symmetry is indicated as $\mathcal{D}^{(2)} \otimes d^{(2)}$, where electrons of angular momentum $L = 2$ interact with vibrations also belonging to an $l = 2$ representation. This system is relevant to the physics of fullerene ions C_{60}^{+}, where the 5-fold degenerate electronic state has H_u icosahedral label and the quadrupolar distortions correspond to some of the h_g modes.[7] It has been shown by different methods and independent groups that, for increasing coupling, a nondegenerate state in the vibronic spectrum moves down, to cross the 5-fold ground state at some finite value of the coupling parameter, thus becoming the ground state at strong coupling .[7,8] This phenomenon is related to the absence of a Berry phase entanglement in the coupled dynamics.[7]

The rôle generally attributed to the Berry phase is therefore to guarantee a "symmetry conservation rule" for the ground state from weak to strong coupling of DJT systems. The absence of this geometrical phase allows the strong-coupling ground state to become the "natural" nondegenerate totally symmetrical representation that a naive picture, ignoring this geometrical phase, would predict in all cases. In this work we reconsider in detail the connection between the symmetry/degeneracy of the vibronic ground state of a large class of DJT systems, and the presence/absence of a Berry phase in the coupled dynamics, finding that the relation sketched above does not apply automatically to all cases.

In the general formalism of the JT effect, a degenerate electronic state corresponding to a representation Γ of the symmetry group $\mathcal{G}$ of the molecule can interact with the vibrational modes corresponding to representations $\{\Lambda\}$ contained in the symmetric part of the direct product $\Gamma \otimes \Gamma$ (excluding the identical representation which is trivial). In the case where exactly one mode of each symmetry label Λ, of frequency ω_Λ and coordinates $q_{\Lambda i}$, interacts linearly with strength g_Λ with the $|\Gamma|$-fold degenerate electronic level (with a fermion operator $c_{\Gamma k}$), the Hamiltonian may be written:

$$H = \frac{1}{2} \sum_{\Lambda} \hbar\omega_\Lambda \sum_{i=1}^{|\Lambda|} (p_{\Lambda i}^2 + q_{\Lambda i}^2) + H_{\mathrm{e-v}} \ , \tag{1}$$

with

$$H_{\mathrm{e-v}} = \frac{1}{2} \sum_{\Lambda} g_\Lambda \hbar\omega_\Lambda \sum_{i=1}^{|\Lambda|} \sum_{j,k=1}^{|\Gamma|} q_{\Lambda i} c_{\Gamma j}^{\dagger} c_{\Gamma k} \langle \Lambda i | \Gamma j \Gamma k \rangle \ , \tag{2}$$

where $\langle \Lambda i | \Gamma j \Gamma k \rangle$ are the Clebsch-Gordan coefficients for the group $\mathcal{G}$.[11] In

Eq. (1) we choose the real representation for the vibrational degrees of freedom, and a second-quantized notation for the electrons.

In the general case of arbitrary frequencies ω_Λ and couplings g_Λ, the point group symmetry $\mathcal{G}$ is reflected in the JTM, constituted of isolated minima, separated by saddle points. However, the continuous JTM of the special equal-coupling equal-frequencies case is invariant for transformations in the group $SO(|\Gamma|)$ of the electronic manifold. Indeed, the whole problem reduces to a single-mode JT coupling between two representations of that group of $|\Gamma|$-dimensional rotations.[12,13] In such a case, it is well known[14] that the set of minima of the Born-Oppenheimer (BO) potential, corresponding to the most energetically-favorable classical distortions, constitute a continuous manifold, referred to as Jahn-Teller manifold (JTM). The JT coupling induces an adiabatic mapping of the vibrational space into the electronic space. Here we only sketch this mapping, which is described in greater detail elsewhere.[15]

In the traditional BO scheme there are assumed much larger separations between consecutive electronic levels than the typical vibrational energies $\hbar\omega$. In a JT problem, each electronic eigenvector $|\psi_\xi\rangle$ of the coupling matrix (2), of eigenvalue λ_ξ, generates a BO potential sheet $V_\xi(\vec{q})$. At strong coupling g, the separation of the potential sheets becomes so large that the adiabatic motion can be safely assumed to always follow the lowest BO potential sheet, while virtual electronic excitations may be treated as a small correction.

On the other side, due to time-reversal invariance of H, the space of all possible (normalized) electronic eigenstates can be represented by an (hyper-)sphere in the $|\Gamma|$-dimensional real space (see Fig. 1). The BO dynamics realizes an adiabatic mapping of the vibrational space into this electronic sphere:[14] every point $\vec{q}$ on the JTM (in the vibrational space) is associated to the electronic wave function $|\psi_{\min}(\vec{q})\rangle$, corresponding to the lowest eigenvalue $\lambda_{\min}$ of the interaction matrix.

This adiabatic mapping is two-valued, since opposite points $\pm|\psi_{\min}(\vec{q})\rangle$ on the electronic sphere give the same JT stabilization energy, thus corresponding to the same optimal distortion on the JTM. This identification of the antipodal points through the mapping is the mechanism allowing the JTM to have a different (topology) with respect to the electronic sphere. The latter is always simply connected, i.e. any closed path on it can be smoothly contracted to a single point. The JTM, instead, may well be multiply connected, i.e. it can have intrinsic "holes" in its topology, related to the nontrivial class of those loops mapped on a path going from a point to its antipode on the electronic sphere, such as π_2 in Fig. 1. This electronic sign change is a case of Berry phase.[9]

This geometric phase acts as a boundary condition for the quantization

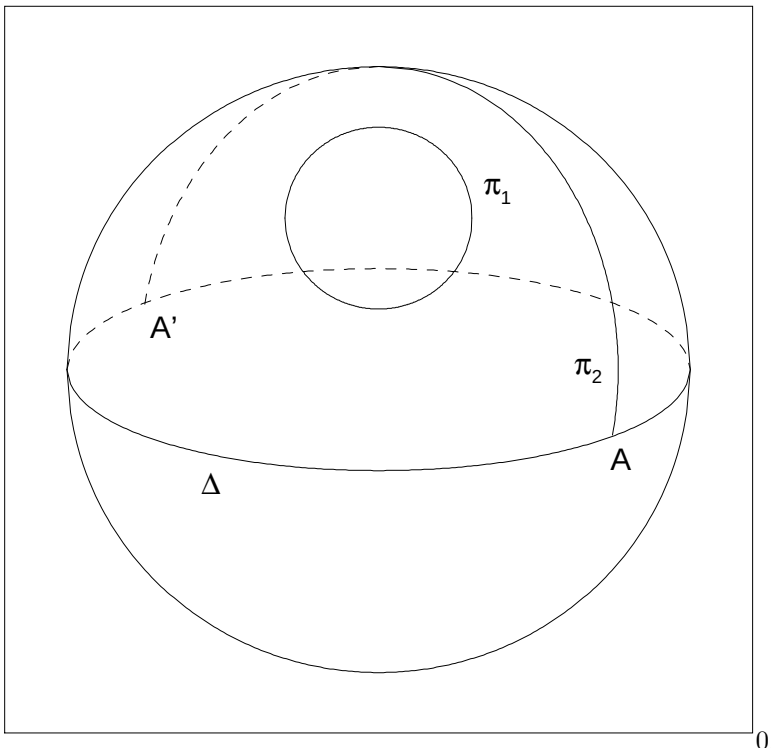

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Figure 1. A sketch of the electronic sphere. The picture individuates the two classes of paths mapping onto closed loops in the JTM: paths of the type π_1 may be contracted continuously to a single point, while those of type π_2 involve a sign change (from A to A') of the electronic state (a Berry phase).

of the vibrational motion. As a consequence, the motion on the JTM is constrained by special selection rules. For example the JTM of the simple $E \otimes e$ system is a circle: the low-energy vibronic spectrum is indeed a j^2 spectrum as for a circular rotor, but the Berry phase implies $j = \pm\frac{1}{2}, \pm\frac{3}{2}, ...$, instead of $j = 0, \pm 1, \pm 2, ...$ as for an ordinary quantum rotor.[2,16] Similarly, the JTM of the $T \otimes h$ (i.e. $\mathcal{D}^{(1)} \otimes d^{(2)}$, in the spherical language) is equivalent to a sphere,[4,17] but out of all the states, labeled by J, M, of a particle on a sphere, the Berry phase retains only the odd-J ones.[2,4,17] Note in particular that in these examples the presence of a Berry phase rules out the "natural" nondegenerate ground state, and enforces, to the strong-coupling DJT ground

state, the same original symmetry Γ of the degenerate electronic state.

The Berry phase, though *not* automatically implied by linear JT Hamiltonians (1), is indeed a very common feature. The double-valuedness of the adiabatic mapping described above is unavoidable. For the Berry-phase–free cases, the mechanism leading to equivalence of the paths in the class 1 and 2 needs to coexist with it. As demonstrated in earlier work,[7,15,18] the solution of the riddle is provided by a point $\vec{q}_d$ *on the JTM* where the mapping is degenerate, i.e. it links $\vec{q}_d$ not just to a pair of opposite points $\pm|\psi_{\min}(\vec{q}_d)\rangle$ on the electronic sphere, but to the whole circle (such as, for example, Δ in Fig. 1) of linear combinations $\cos\theta\,|\psi_1(\vec{q}_d)\rangle + \sin\theta\,|\psi_2(\vec{q}_d)\rangle$ of two degenerate orthogonal electronic eigenstates. Where such a point is present, it allows to deform smoothly any loop of class 2 on the JTM, until its image on the electronic sphere becomes half this circle, thus shrinks to the single point $\vec{q}_d$. All loops are therefore contractable, thus equivalent to one another and, therefore, the JTM is simply connected. No Berry phase is possible in such a case.[15,18]

Such a tangency point is the origin of the inversion of the low-lying levels in the $H \otimes h$ JT problem,[7,15] leading to a nondegenerate ground state at strong coupling. Similar tangential points were demonstrated[15,18] in other spherically symmetric linear models, the $\mathcal{D}^{(L)} \otimes d^{(L)}$, with $L = 2, 4, 6, ...$ All these systems are therefore Berry-phase free, with, in particular, a strong-coupling non-degenerate vibronic ground state. A numerical test confirms this result in the $\mathcal{D}^{(4)} \otimes d^{(4)}$ case. On the contrary, these tangencies are absent in most DJT cases ($E \otimes e$, $T \otimes h$, $\mathcal{D}^{(2)} \otimes d^{(4)}$, ...), whence the Berry phase, whence the degenerate ground state at strong coupling.

The systems $\mathcal{D}^{(L)} \otimes d^{(l)}$, with $L > l$, are remarkable in having a tangency point, thus no Berry phase as the preceding example, but *no symmetry change* of the ground state, which remains degenerate to all couplings.[15] This case should be kept as a warning against the simplistic equation: absence of Berry phase = nondegenerate strong-coupling ground state.

We move on now to the investigation of the relations between ground state symmetry, Berry phases and tangencies of potential sheets in the more general case of $H \otimes (2\,h \oplus g)$ Jahn-Teller coupling in icosahedral symmetry. The two h and the g modes can be classified according to their spherical parentage

$$\begin{aligned} d^{(2)} &\rightarrow h_{[2]} \\ d^{(4)} &\rightarrow h_{[4]} \oplus g\ . \end{aligned} \tag{3}$$

The existence of two different couplings $g_{h_{[2]}}$ and $g_{h_{[4]}}$ to modes h reflects the fact that the icosahedral group is not simply reducible:[19] two independent sets of Clebsch-Gordan coefficients for the coupling of h and h to h are necessary.[8,11,20] In the special case when $\omega_{h_{[4]}} = \omega_g = \omega_4$ and $g_{h_{[4]}} = g_g = g_4$

the $SO(3)$ symmetry of the linear problem is restored, and it can be labeled accordingly: $\mathcal{D}^{(2)} \otimes (d^{(2)} \oplus d^{(4)})$). In the limit $g_4 = 0$ we recover the Berry-phase–free $\mathcal{D}^{(2)} \otimes d^{(2)}$ model discussed above.

In the completely equal-coupling equal-frequencies limiting case $\omega_4 = \omega_2$ and $g_4 = g_2$, as anticipated above for the general case, the symmetry rises further to $SO(5)$:[13] the model may be described as $[1,0] \otimes [2,0]$ in the notation of $SO(5)$ representations. For the equal-coupling case, the presence of a Berry phase has been explicitly demonstrated,[7] together with its consequences for the selection rules on the levels: it favors in the low-energy end of the spectrum $[k,0]$ levels with odd k. In particular, it was verified that the ground state remains 5-fold degenerate ($[1,0]$ in $SO(5)$ notation, i.e. $\mathcal{D}^{(2)}$ as a $SO(3)$ representation), and the first excited is a 30-fold degenerate $[3,0]$ level.

In the general case $g_2 \neq g_4$, the symmetry reduces to $SO(3)$, thus the large $SO(5)$ representations split into their spherical components. In sweeping the value of g_4 from g_2 down to 0, the system passes smoothly from a regular Berry-phase–related degenerate ground state to the $\mathcal{D}^{(2)} \otimes d^{(2)}$ Berry-phase–free nondegenerate ground state (for large enough g_2). In this final situation, the degenerate $\mathcal{D}^{(2)}$ state takes the rôle of the lowest excited state, separated by a finite energy gap from the nondegenerate $\mathcal{D}^{(0)}$ ground state.[7,8] Thus, a level crossing takes place between the low-lying levels, at some intermediate value of g_4: we can define a crossover value g_4^{c} (dependent on g_2) for which the ground-state symmetry changes. At strong coupling, the energy gap $E[L = 2] - E[L = 0] = c_2/g_2^2 + O(g_2^{-4})$ for $g_4 = 0$ and $E[L = 2] - E[L = 0] = -c_4/g_4^2 + O(g_4^{-4})$ for $g_2 = 0$, where c_2 and c_4 are positive constants depending on ω_2 and ω_4. Thus, the crossover curve $(g_2, g_4^{\mathrm{c}}(g_2))$ should get asymptotically close to the straight line $g_4 = g_2 (c_4/c_2)^{1/2}$ in the plane of the coupling parameters.

These considerations, as well as some exact diagonalizations on a truncated basis, permit to draw the qualitative zero-temperature "phase diagram" represented in Fig. 2. It strikes for containing a whole region $(0 < g_4 < g_4^{\mathrm{c}}(g_2))$ where a nondegenerate $L = 0$ ground state coexists with the presence of a Berry phase. This example should stand as a warning against the simplistic equation: Berry phase = degenerate strong-coupling ground state of the same symmetry as the non-interacting electronic state. We conclude, accordingly, that the presence of a Berry phase in many-mode DJT systems is *not a sufficient condition* for the degeneracy of the ground state. Indeed, even if the overall system has a phase entanglement, the absence of a Berry phase in one of the single-mode couplings allows for a non-degenerate ground state in some regions of the coupling-parameters space.

At this point it is necessary to reconcile the gradual, smooth lowering of the nondegenerate state as g_4/g_2 is reduced from equal coupling towards

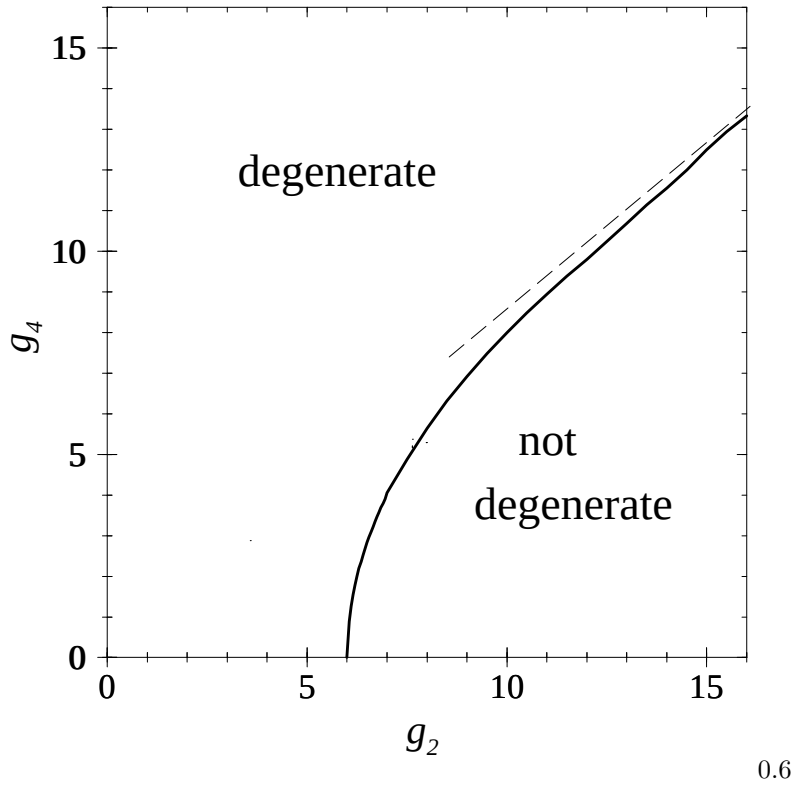

Figure 2. The zero-temperature "phase diagram" of the $\mathcal{D}^{(2)} \otimes (d^{(2)} \oplus d^{(4)})$ JT system in the space of the coupling parameters g_2 and g_4, for fixed frequencies ω_2 and ω_4. At the solid line $g_4 = g_4^c$ the $L = 0$ and $L = 2$ ground states become (accidentally) degenerate.

zero, with the abrupt disappearance of the Berry phase (which is a topological effect, intrinsically non-perturbative) for $g_4 = 0$. The origin of the nondegenerate state is to be traced back to the 30-fold degenerate first-excited state ($[3, 0]$ according to $SO(5)$) of the equal-coupling "hypersymmetrical" spectrum which splits into its $L = 0, 3, 4, 6$ components ($SO(3)$ representations) as soon as $g_4 \neq g_2$. In particular, this $L = 0$ fragment is the lowest when $g_4/g_2 < 1$. For small enough g_4/g_2, this nondegenerate state has the opportunity to localize as much as possible in the potential well in the $d^{(2)}$ vibron space (corresponding to the JTM in the space of $d^{(2)}$ vibrations), eventually crossing down below the $L = 2$ ground state, to become itself the ground

state. Even in this region, however, the Berry-phase prescription in the $SO(5)$ language is respected, since the $L = 0$ state is indeed a fragment of an odd ($[3, 0]$) – Berry-phase allowed – level: the ground state still fulfills the parity constraint imposed to the low-energy $SO(5)$ representations by the Berry phase in the global space.

Note, incidentally, that, although the $\mathcal{D}^{(2)} \otimes d^{(2)}$ problem is only $SO(3)$-symmetric, its JTM has $SO(5)$ symmetry. Therefore, in the limit of infinitely large g_2 and vanishing g_4, where the motion is essentially restricted to the JTM in the $d^{(2)}$ vibration space, that same nondegenerate ground state may also be classified as an $[0, 0]$ state for the symmetry group of the JTM, where it complies therefore with the absence of Berry phase.

As a first remark, we note that our treatment calls for a revision of the customary association of Berry's phase to a breakdown of the BO approximation. Indeed, the geometrical phase originates at the conical intersections of the lowest two BO sheets. At strong coupling, such points lie at high energy and the system explores them with extremely small probability. On the contrary, here we relate the *absence* of the geometrical phase to tangential contacts of the adiabatic sheets, *on the JTM*, thus affecting low-potential regions which the system occupies currently. Thus, in these systems, it is not the Berry phase which is connected to a breakdown of the BO approximation, but its absence.

Our analysis considers for simplicity spherical DJT models: however, it can be extended to molecular point groups. For example, the Berry phase and ground-state symmetry switch of the $H \otimes \left(h_{[2]} + h_{[4]}\right)$ are completely analogous to those of $\mathcal{D}^{(2)} \otimes (d^{(2)} \oplus d^{(4)})$ described above.[8]

Also, we assume a linear JT coupling scheme (Hamiltonian (1)), which is the less realistic, the stronger the JT distortion. The introduction of quadratic and higher-order couplings has usually effects similar to those produced by unequal linear couplings and/or frequencies in $T \otimes (e + h)$ in cubic symmetry,[21] i.e. of "warping" the JTM, reducing its symmetry. Yet, the connectedness properties are topological properties, thus robust against warping, as long as it can be treated as a perturbations. To quote the simplest example, the introduction of quadratic terms in the $e \otimes E$ Hamiltonian[22] does not substantially change the picture as far as the Berry phase and the symmetry/degeneracy of the ground state are concerned. In fact, even at strong JT coupling, the tunneling among rather deep isolated minima is affected by the electronic phase,[2] and, as a result, the lowest tunnel-split state retains the same symmetry and degeneracy as in the purely linear-coupling case. Of course, if the quadratic and higher-order couplings dominate over the linear term, new conical intersections may appear, thus affecting the Berry phase and, consequently the

ground-state symmetry.[23]

In summary, the standard rôle of the Berry phase is to guarantee a "symmetry conservation rule" for the ground state from weak to strong coupling of linear DJT systems. Here, we propose two counterexamples to this simple pattern: (i) a whole family, of Berry-phase–free dynamical JT systems with a *degenerate* ground state at all couplings, the $\mathcal{D}^{(L)} \otimes d^{(l)}$ models, with $l < L$; and (ii) the case of many modes coupled at the same time to an electronic state, some with a Berry phase entanglement, and some without it, in the region where the coupling to the seconds prevail, the strong-coupling ground state can switch to nondegenerate, as we illustrate for $\mathcal{D}^{(2)} \otimes (d^{(2)} \oplus d^{(4)})$. This second point, in particular, for those cases, such as positive fullerene ions, where Berry-phase–free modes are present, underlines the relevance of the actual values of the coupling strengths between degenerate electrons and vibrations, which only permit to make a prevision about the actual symmetry of the vibronic ground state. In this perspective, the experimental or *ab-initio* determination of the detailed values of such couplings is of the utmost importance for this class of systems. Finally, the rôle of the Berry phase being that of ordering the strong-coupling spectrum, it is conceivable a system where the geometric phase enforces a non-totally symmetrical vibronic state of *symmetry other than* Γ, that of the original electronic state: further investigation od the icosahedral JT zoology may find a realization of this possibility.

Acknowledgement

We thank Arnout Ceulemans, Brian R. Judd, Erio Tosatti, and Lu Yu for useful discussions.

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